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PREPARATION OF A DICOORDINATE SULPHUR DICTATION.(U)
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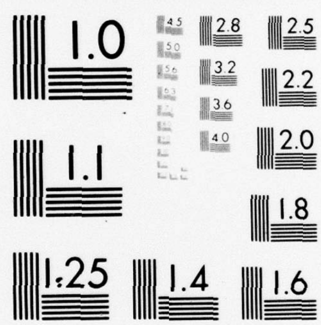

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The first dicoordinate sulphur dication, $(Me_2N)_2S^{2+}$, has been prepared by treatment of $(Me_2N)_2SF_2$ with fluoride ion acceptors.

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PREPARATION OF A DICOORDINATE SULPHUR DICATION

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Summary The first dicoordinate sulphur dication, $(Me_2N)_2S^{2+}$, ← (2+)
has been prepared by treatment of $(Me_2N)_2SF_2$ with fluoride ion acceptors.

THE isoelectronic principle suggests the existence of several six-electron main-group cations such as R_3Si^+, R_3P^{2+}, R_2P^+, and R_2S^{2+}. Thus far only phosphenium (R_2P^+) ions have been found to exist in the condensed phases,[1,2] although, of course, silicenium ions are well known species in the vapour phase.[3] Two-coordinate sulphur dications, R_2S^{2+}, have been postulated as one of the possible transition states involved in the racemisation of sulphonium cations,[4] however, such compounds have never been isolated previously.

Treatment of $(Me_2N)_2SF_2$ (**1**) with one equivalent of a fluoride ion acceptor such as PF_5, AsF_5, or BF_3 in SO_2 solution results in the generation of the cation $(Me_2N)_2SF^+$ (**2**) as described previously.[5] However, when an excess of AsF_5 is employed the ^1H resonance of **2** (doublet, δ 2.95, J_{FSNCH} = 7.0 Hz) was replaced by a singlet at lower field (δ, 3.75) which we assign to the dicoordinate sulphur dication, $(Me_2N)_2S^{2+}$ (**3**). The ^{13}C resonance of **3** singlet (41.6 p.p.m.) was also downfield

of that of 2 (singlet, 37.9 p.p.m.). Moreover, no ^{19}F resonance attributable to 3 could be detected. Particularly compelling is the fact that two anion resonances were detected by NMR when the fluoride ion abstraction from 1 was conducted with two F^- acceptors. For example, treatment of 1 with one equivalent of PF_5 followed by one equivalent of AsF_5 resulted in the detection of PF_6^- (^{31}P: septet, 144 p.p.m., J_{PF} = 711 Hz, ^{19}F: doublet, 72.5 p.p.m., J_{PF} = 711 Hz), AsF_6^- (^{19}F: quartet,[†] 59.4 p.p.m.); and 3.

Vibrational spectroscopy has also been useful for the characterisation of 3. Since $(Me_2N)_2P^+$ and 3 are isoelectronic the vibrational spectra of these cations are expected to be somewhat similar. This is indeed the case. For example, $(Me_2N)_2P^+$ exhibits strong Raman peaks at 997 and 1300 cm^{-1} while for 3 peaks of very similar appearance and relative intensity are observed at 961 and 1247 cm^{-1}. Parry and co-workers[1] have detected peaks at 996 and 1309 cm^{-1} in the infrared spectrum of $(Me_2N)_2P^+$ and assigned them to CN···P stretching. When 3 is generated by treating 1 with 2 equivalents of PF_5 a strong Raman peak at 742 cm^{-1} is detected which has been assigned[6] to $\nu_1(A_{1g})$ of PF_6^-. Similarly, when AsF_5 is used as the fluoride ion acceptor, an analogous band at 685 cm^{-1} is detected which is characteristic[6] of AsF_6^-. When 1 is treated with equimolar quantities of PF_5 and AsF_5 the $\nu_1(A_{1g})$ modes of both PF_6^- and AsF_6^- are detected.

We thank the Office of Naval Research for financial support.

References and Footnotes

†The quartet is due to quadrupolar broadened coupling with the ^{75}As nucleus, $I = 3/2$.

[1]See, for example, M. G. Thomas, C. W. Schultz, and R. W. Parry, *Inorg. Chem.*, 1977, **16**, 994, and references therein.

[2]For characterization by X-ray crystallography, see A. H. Cowley, M. C. Cushner, and J. S. Szobota, *J. Amer. Chem. Soc.*, 1978, **100**, 7784.

[3]See, for example, M. K. Murphy and J. C. Beauchamp, *J. Amer. Chem. Soc.*, 1976, **98**, 5781; M. K. Murphy and J. L. Beauchamp, *ibid.*, 1977, **99**, 2085; Y. Apeloig and P. v. R. Schleyer, *Tetrahedron Lett.*, 1977, 4687.

[4]S. Oae, *Quarterly Reports on Sulfur Chemistry*, 1970, **5**, 53.

[5]A. H. Cowley, D. J. Pagel, and M. L. Walker, *J. Amer. Chem. Soc.*, 1978, **100**, 7065.

[6]G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, 1967, **6**, 2212.

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